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(54) POLYESTER COMPOSITIONS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to compositions containing poly(ethylene terephthalate) which may be converted to shaped articles of improved impact strength.
- Poly(ethylene terephthalate), when of sufficiently high molecular weight, is a high melting readily crystallisable polymer which has found extensive use as a film- and fibre-forming material. Its success in these applications has been due at least in part to the considerable improvement in physical properties that can be obtained by stretching the films and fibres whereby the polymer is obtained in an oriented crystallised form of advantageous morphology. When converted by melt-shaping to articles having one or more sections of a thickness such that they are not easily susceptible to stretching operations, however, the polymer is present in either an amorphous form which is metastable to temperature or an unoriented crystalline form of generally unsatisfactory morphology which is reflected in low impact strength.
- We have now developed a composition which may be converted to shaped articles of improved impact strength.
- According to the present invention, the composition comprises
- (i) poly(ethylene terephthalate),
 - (ii) a rubbery material comprising at least one amorphous or poorly crystalline high molecular weight synthetic polymer or copolymer which is substantially insoluble in poly(ethylene terephthalate) so as to form a discrete dispersed phase therein and which has a glass/rubber transition temperature below 0°C and a dynamic shear modulus not greater than 5×10^9 dynes/cm², and
 - (iii) at least one polyfunctional compound, by which we mean a compound which is (or under the conditions of the melt-shaping process is dissociable to a compound which is) capable of reaction with at least two groups selected from —OH and —COOH groups in poly(ethylene terephthalate) under the conditions of the melt-shaping process,
- and wherein (ii) forms from 1 to 50% of the total weight of (i), (ii) and (iii).
- The composition may be converted to a shaped article by melt-shaping and to achieve the desired benefit it is necessary that the preparation of the composition and conversion thereof to the shaped article are conducted such that in the shaped articles so obtained the rubbery material is present in the form of finely dispersed discrete particles.
- By melt-shaping we mean shaping the composition, e.g. by pressing it into a mould or passing it through a die (for example of an extruder) while at a temperature above the melting point of the poly(ethylene terephthalate).

ate) and then causing or allowing it to cool below said melting point while in contact with the shape-conferring surface or surfaces. Examples of such melt-shaping processes are extrusion, melt-casting and compression moulding. Much the preferred process, however, is injection-moulding.

In the melt shaped products obtained from these compositions, groups each comprising two or more individual chains of the poly(ethylene terephthalate) have become linked together by molecules of the polyfunctional compound to form chain-extended ethylene terephthalate polymer, by which we mean a polymer comprising macromolecular units each formed of at least two polymeric chains each consisting essentially of recurring ethylene terephthalate mers (that is, at least 90% of the mers forming the polymeric chain have the structure



where Ar represents a para-phenylene group) each chain being linked to another chain by a chemically different mer, which mer is derived from the polyfunctional compound. The shaped article, therefore, comprises a matrix of chain-extended ethylene terephthalate polymer having particles of rubbery material finely dispersed in it.

By the term poly(ethylene terephthalate), as used with reference to the compositions of this invention, we mean not only the homopolymer of ethylene glycol and terephthalic acid but also copolymers wherein, for example, some of the ethylene glycol residues are replaced by other diol residues, e.g. diethylene glycol, and/or some of the terephthalic acid residues are replaced by other dicarboxylic residues, e.g. isophthalic acid, provided that the ethylene terephthalate residues form at least 90 mole % of the polymer chain. It is generally preferred to use the homopolymer, however.

It is preferred that the poly(ethylene terephthalate) used in our compositions has a molecular weight corresponding to an intrinsic viscosity, as hereinafter defined, of at least 0.4 decilitre/gram, as measured in o-chlorophenol at 25°C, and more preferably at least 0.6 decilitre/gram, in order to provide shaped articles of desirable physical properties. Poly(ethylene terephthalate) of very high molecular weight, on the other hand, may prove difficult to mould because of its very high viscosity in the melt.

By intrinsic viscosity we mean the value obtained by plotting values of the fraction

$$\frac{t - t_0}{t_0 c}$$

where t is the flow time of a "c" gram decilitre⁻¹ solution of the polymer in a given sol-

vent using a standard viscometer, and t_0 is the flow time of the same volume of pure solvent through the same viscometer under the same conditions, against the concentration c for various values of c , and extrapolating the curve obtained to zero concentration. All figures for intrinsic viscosity in this specification as based on measurements derived from solutions of the polymer in o-chlorophenol at 25°. The fraction identified above is sometimes known as the reduced viscosity for a given solution concentration.

To be suitable as the rubbery material for use in our invention, the synthetic high molecular weight polymer or copolymer must satisfy the following requirements:

(1) It must be amorphous or at most only poorly crystalline, by which we mean that it exhibits no more than weak crystallinity on X-ray examination. That is, the crystallinity pattern, if any, consists of a series of diffuse bands.

(2) It must have a glass/rubber transition temperature below 0°C., measured by differential thermal analysis at a rate of change of temperature of 5°C or less per minute.

(3) It must have a dynamic shear modulus not greater than 5×10^9 dynes/sq.cm. The dynamic shear modulus is measured at 20°C by the torsion pendulum method using a frequency of about 1 cycle per second.

(4) It must be substantially insoluble in poly(ethylene terephthalate) so as to form a discrete dispersed phase therein. In general, it may be said that if the calculated solubility parameter of the copolymer differs from that of poly(ethylene terephthalate) by more than 0.2, it will be substantially insoluble therein. The solubility parameter is calculated by the method according to Small as described in the Journal of Applied Chemistry, Volume 3, 1953, pages 71 to 80.

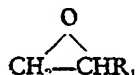
The polymer or copolymer must also, of course, be able to withstand the temperature at which shaping is carried out without deteriorating to such an extent as to render the shaped products valueless. Optionally, it may be branched and/or crosslinked to a degree sufficient to prevent severe distortion of the rubber particles during fabrication of the composition.

Preferably, the rubbery material will have groups in or on its macromolecular chains capable of reaction with the polyfunctional compound under the conditions of the melt shaping process, in which case at least some of the particles of the disperse phase in the articles so produced will be grafted on to the chain-extended ethylene terephthalate polymer matrix by means of molecules of the polyfunctional compound and the shaped articles so obtained generally exhibit particularly useful improvements in impact strength. Such grafting may be detected by exhaustively extracting a sample of the shaped article in

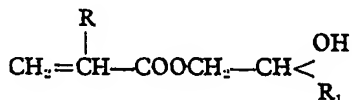
o-chlorophenol. If the existence of poly-(ethylene terephthalate) can be detected in the residue by infra-red examination, then grafting has occurred. By exhaustive extraction we mean extraction until no further reduction in weight of the residue occurs.

It has been found, however, that desirable improvements in toughness may be obtained even where the rubbery material is not capable of reaction with the polyfunctional compound or compounds in the composition.

Examples of groups which may be reactive with the polyfunctional compound include hydroxy and carboxylic —OH groups, amino groups both primary and secondary, thiol groups, anhydride groups and epoxy groups. Synthetic rubbery materials having —OH groups pendant from the macromolecular chains, e.g. as in hydrolysed ethylene/vinyl acetate copolymers, are preferred but because of the ease with which they may be processed and their ready reactivity with polyisocyanates, which are the preferred polyfunctional compounds, we particularly prefer to use rubbery copolymers of ethylene and, as at least one of the comonomers polymerised therewith, a hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid, especially acrylic acid or methacrylic acid. Hydroxyalkyl esters of these acids are conveniently obtained by reacting them with ethylene oxide or a higher alkylene-1,2-oxide. The product from ethylene oxide is the 2-hydroxyethyl ester; the products from a higher oxide having the structure

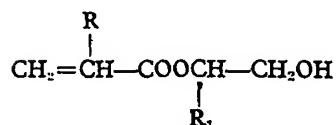


where R_1 is an alkyl group will be one or both of the compounds having the structures



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and



in which R is H (in acrylic acid) or CH_3 (in methacrylic acid). Thus, in the case of the reaction of propylene oxide, for example, the product is either one, or a mixture of both, of the 2-hydroxy-n-propyl ester and the hydroxy isopropyl ester.

Examples of such copolymers are those of ethylene with 2-hydroxyethyl methacrylate

(obtained from the reaction of ethylene oxide and methacrylic acid, for example), of ethylene with one or more of the appropriate hydroxypropyl methacrylates (obtained from the reaction of propylene oxide and methacrylic acid), and of ethylene with methyl methacrylate and one or more of said hydroxypropyl methacrylates.

Examples of other synthetic rubbery materials that may be used may be found in particular among polyisobutylene, and random copolymers of ethylene with propylene, or with propylene and a non-conjugated diene, or with one or more esters of acrylic and/or methacrylic acids with, for example, alcohols containing up to 8 carbon atoms, and/or with one or more vinyl alkanoates; for example copolymers of ethylene with methyl methacrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate and/or vinyl acetate.

The amount of rubbery material used in the composition is from 1 to 50%, by weight of the sum of the amounts of the poly(ethylene terephthalate), the polyfunctional compound and the rubbery material. With the use of amounts below 1%, little or no advantage is obtained but at amounts in excess of about 50%, an inversion of the phases may occur with a tendency for the ethylene terephthalate polymer to be dispersed in a matrix of rubber and for the modulus of the shaped articles to drop markedly. In general, it is preferred to use from 5% to 35%, and especially from 5% to 15%, such amounts providing the optimum balance of toughness and modulus in the shaped articles.

The polyfunctional compound found in the compositions of our invention is characterised by having, or being thermally or otherwise dissociable to a compound having one or more functional components such that it is capable of reacting with at least two groups each of which is either —OH or —COOH. Examples of such functional components are carboxylic acid groups; carboxylic acid anhydride groups; acid halide groups, e.g. acid chloride and acid bromide groups; epoxide groups; and isocyanate groups.

Preferred examples of polyfunctional compounds that may be used are poly(carboxylic acid anhydrides), polyepoxides, polyisocyanates and compounds which are thermally or otherwise dissociable under the conditions of the shaping process to polyisocyanates, hereinafter referred to as polyisocyanate generators. By the terms poly(carboxylic acid anhydrides), polyepoxides and polyisocyanates, we mean organic compounds containing two or more carboxylic acid anhydride (—CO.O.CO—), epoxide and isocyanate groups, respectively.

It is preferred to use those polyfunctional compounds which are not highly volatile at the processing temperatures and it is particularly preferable to use those that will react

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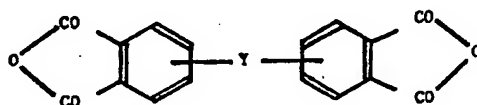
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with the minimum of by-product formation. Especial examples of the latter group are those compounds with isocyanate, epoxide and/or anhydride groups as functional components, and uretidione dimers and higher molecular weight uretidione oligomers of polyisocyanates.

- The use of poly(carboxylic acid anhydrides), e.g. of tetra- or higher-functional carboxylic acids, is noteworthy where it is especially desirable to avoid discolouration in the shaped articles. Examples of the preferred aromatic compounds are pyromellitic acid dianhydride; naphthalene tetracarboxylic acid dianhydrides such as the 1,4,5,8-, 2,3,6,7- and 1,2,5,6-isomers; mellitic acid trianhydride; perylene-3,4,9,10-tetracarboxylic acid dianhydride; and dianhydrides having the structure:



- where Y is a direct link, $-\text{O}-$, $-\text{SO}_2-$, $-\text{CO}-$, or divalent hydrocarbon e.g. $-\text{CH}_2-$ or $-\text{C}(\text{CH}_3)_2-$; for example 3,3', 4,4'-biphenyl tetracarboxylic acid dianhydride and its 2,2', 3,3'-isomer; bis(3,4-dicarboxyphenyl) alkane dianhydrides e.g. the dianhydride of 2,2 - bis(3,4 - dicarboxyphenyl)propane; bis(3,4 - dicarboxyphenyl)sulphone dianhydride; bis(3,4 - dicarboxyphenyl)ether dianhydride and benzophenone - 3,3', 4,4' - tetracarboxylic acid dianhydride. Ethylene tetracarboxylic acid dianhydride may also be mentioned. The much preferred polyanhydride is pyromellitic acid dianhydride.

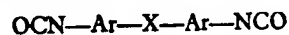
- Preferably, the polyfunctional compound contains groups which are capable of reacting with both $-\text{OH}$ and $-\text{COOH}$ groups. In this class, polyisocyanates and polyisocyanate generators are especially noteworthy since not only do they react (or, on heating, yield compounds which react) with both $-\text{OH}$ and $-\text{COOH}$ groups to give urethane and amide linkages respectively but they may also react with the linkages so formed, e.g. to form acylurea and allophanate links. Potentially much greater improvements in physical properties may be obtained from the use of these compounds than from the use of the other polyfunctional compounds named above.

- Examples of diisocyanates are (a) polymethylene diisocyanates, e.g. those having the structure



- where n is a positive integer, for example from 4 to 20, examples being tetramethylene diisocyanate, hexamethylene diisocyanate, dodecamethylene diisocyanate and eicosane 1,20-diisocyanate; (b) derivatives of these compounds wherein one or more of the hydrogen

atoms of the methylene groups are replaced by monovalent hydrocarbyl groups, e.g. 4-butylohexamethylene diisocyanate or 2,2,4 and 2,4,4 - trimethylhexamethylene diisocyanates; (c) derivatives of (a) or (b) wherein one or more of non-adjacent methylene groups are replaced by $-\text{O}-$, $-\text{S}-$ or $-\text{NR}-$ where R is hydrogen or monovalent hydrocarbon e.g. $\text{OCN}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{NCO}$; (d) mononuclear and fused polynuclear diisocyanates, e.g. toluene - 2,4 - diisocyanate, p - phenylene diisocyanate, xylylene diisocyanates, 3 - isocyanatomethyl - 3,5,5 - trimethylcyclohexyl isocyanate and naphthalene diisocyanates; (e) sulphonyl diisocyanates; (f) silicon and phosphorus diisocyanates; and, especially, (g) diisocyanates having the structure



where each Ar is a divalent, preferably mononuclear, aromatic nucleus in which one or more of the hydrogen atoms may, if desired, be replaced by inert monovalent groups, e.g. alkyl, alkoxy or halogen, and X is a direct linkage or a divalent atom or group, e.g. $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{SO}-$, $-\text{NR}'-$ (where R' is monovalent hydrocarbon), $-\text{CO}-$ and divalent hydrocarbon, e.g. alkylene. Examples of (g) are the 3,3' - 4,4' - and 3,4' - diisocyanates of diphenylmethane, 2,2-diphenylpropane and diphenyl ether; 3,3'-dimethyl - 4,4' diisocyanatobiphenyl and 3,3' - dimethoxy - 4,4' - diisocyanato biphenyl. 4,4' - diisocyanatobiphenyl methane gives good results and is readily available.

Where it is desired to use a diisocyanate and the colour of the product is important, it has been found profitable to use compounds which are substantially involatile under the reaction conditions and wherein the isocyanate groups are attached to non-aromatic carbon atoms, e.g. as in 4,4' - diisocyanatodicyclohexylmethane isomers and mixtures thereof, 2,5 - dimethyl - p - xylylene diisocyanate, 1,4 - di(2 - isocyanatoethyl) - 2,5 - dimethylbenzene and tetramethyl - p - xylylene diisocyanate. In general, however, when these are used, the compositions require somewhat longer dwell times in the melt during the shaping process than is the case with aromatic diisocyanates, unless a catalyst is added.

Examples of diisocyanate generators are the following derivatives of diisocyanates: polymeric urethanes, uretidione dimers and higher oligomers, cyanurate polymers, urethanes and polymeric urethanes of cyanurate polymers, and thermally dissociable Schiff's base adducts. Particularly preferred examples are uretidione dimers and higher oligomers, e.g. the uretidione dimer and higher oligomers of diisocyanates of type (g) and especially of 4,4'-diisocyanatodiphenyl methane.

The amount of polyfunctional compound suitable for incorporation in the compositions

of the present invention depends in part upon its nature. Where it is capable of reaction with only —OH and/or —COOH groups the maximum improvement in properties is generally achieved when just sufficient polyfunctional compound is present to react with all such groups, quantities above and below this quantity usually resulting in reduction of the advantage obtained. On the other hand, if the polyfunctional compound is capable of reaction not only with —COOH and —OH groups but also with the products of such reactions, for example as in the case of polyisocyanates and derivatives thereof, proportions considerably in excess of the stoichiometric amount based on the number of groups in the initial composition which are reactive with isocyanate groups may be advantageously included in the compositions. The amount to be used is also a function of the relationship between the intrinsic viscosity of the poly(ethylene terephthalate) in the composition to be shaped and the desired intrinsic viscosity of the chain-extended ethylene terephthalate polymer matrix in the articles shaped from the composition. In general, the higher the intrinsic viscosity required in the matrix in a shaped article produced from poly(ethylene terephthalate) of a particular intrinsic viscosity, the more polyfunctional compound will be required. Also, the lower the intrinsic viscosity of the poly(ethylene terephthalate) the more polyfunctional compound is required to produce a given increase in intrinsic viscosity.

In the preferred case where the rubbery material is capable of reacting with the polyfunctional compound, the composition may advantageously accommodate an excess of polyfunctional compound over and above that desired for reaction with the poly(ethylene terephthalate).

The particular quantities of polyfunctional compound required in any individual case may be determined by simple experiment but in general 0.05% to 10% by weight of the mixture of polymer, rubbery material and polyfunctional compound has been found suitable for most circumstances with a preference for the use of about 0.5 to 5%.

The compositions of our invention may be prepared by any conventional blending techniques, but preferably by melting a mixture of poly(ethylene terephthalate), rubbery material and polyfunctional compound and subjecting the mixture to mechanical mixing action, for example in an extruder, in the screw of screw-fed injection-moulding apparatus, or on a mill.

Alternatively, for example, the components of the composition may be dissolved in a suitable solvent, for example diphenyl ether, nitrobenzene or tetrahydrothiophene-1,1-dioxide, the solutions mixed and either the solvent removed, for example by evaporation, or the composition precipitated, for example

by pouring the solution into a non-solvent for all the components.

The components of the composition may be mixed in a single operation or, if desired, in two or more separate operations. For example, the poly(ethylene terephthalate), polyfunctional compound and rubbery material may all be mixed together, e.g. in an extruder or in the screw of a screw-fed objection-moulding apparatus. Improved results may be obtained, however, if the poly(ethylene terephthalate) and the rubbery material are melt-blended before the polyfunctional compound is added. For example, the poly(ethylene terephthalate) and rubbery material may be melt-blended together in an extruder and the polyfunctional compound then melt blended with the resultant extrudate, e.g. in a further extrusion which, if desired, may be effected in a screw-fed injection-moulding apparatus. In another alternative, the poly(ethylene terephthalate) may be mixed with rubbery material, with the latter in a proportion in excess of that desired in the final composition, in for example a screw extruder, and subsequently mixed with further poly(ethylene terephthalate) and polyfunctional compound, for example in a further extrusion which, if desired, may be effected in the screw of a screw-fed injection-moulding machine. Other ways of forming the compositions will be apparent to those skilled in the art.

The compositions may be converted to shaped articles by any suitable melt-shaping process provided that in the resultant shaped article the rubbery material is found in the form of discrete particles finely dispersed in the chain-extended ethylene terephthalate polymer matrix. The required dispersion may be achieved during the formation of the composition or during the melt-shaping thereof. The production of this dispersion may be achieved, for example, by dissolving the components in a suitable solvent and reprecipitating. More conveniently, however, it may be achieved by subjecting the mixture of poly(ethylene terephthalate) and rubbery material to a suitable degree of shear. This may be effected at some stage during the formation of the composition, e.g. in the screw of an extruder. Alternatively, or additionally, it may be effected in the shaping apparatus itself, e.g. in the screw of a screw-fed injection-moulding machine or of a screw-extruder. Preferably the average size of the rubbery particles in the shaped article is 10 microns or less, e.g. 0.5 to 10 microns, since then very useful improvements in impact strength are obtained. If the size is too small, however, the improvement in impact strength may be reduced. Control of the particle size may be achieved, for example, by variation of the extent of the shear imparted to the mixture, e.g. by altering the viscosity of the mixture by changing its temperature or by altering other conditions of extrusion.

Another factor controlling the improvement in impact strength obtained by our invention is the intrinsic viscosity of the chain-extended ethylene terephthalate polymer in the shaped article. Preferably this is at least 0.5 decilitre gram⁻¹ and most preferably 0.65 to 0.85 decilitre gram⁻¹. The value of the intrinsic viscosity depends mainly upon the temperatures to which the poly(ethylene terephthalate) is subjected in the molten state in the presence of the polyfunctional compound with which it reacts, and the overall times for which it is exposed to those temperatures. In general, the initial trend is for the intrinsic viscosity of the chain-extended polymer matrix to increase with time, the rate of increase being in general greater at higher temperatures. However, after an initial period, the duration of which depends upon the amount of polyfunctional compound present and the temperature to which the composition is subjected, the intrinsic viscosity reaches a maximum and, because of competing thermal degradation reactions, thereafter declines with consequent adverse effect upon the physical properties of the product. In general, as the temperature is increased, both the time to reach maximum intrinsic viscosity and the maximum achievable intrinsic viscosity are decreased; it is therefore preferred to avoid the use of high temperatures or extended dwell times in the mixing and shaping processes. Temperatures of from 255°C to 290°C are preferred with overall dwell times of from 30 seconds to 15 minutes at these temperatures.

The rate of change of intrinsic viscosity with time is also controlled by the concentration of polyfunctional compound the increase of which tends to increase the period required to achieve maximum effect but, above the optimum value, may reduce the maximum attainable extent of the effect.

Where the rubbery material is reactive with the polyfunctional compound, the effect of varying the fabrication conditions upon the ultimate properties of the shaped product, however, is generally less marked, thus allowing more flexibility of operation.

The benefit of the invention may be obtained whether the matrix in the shaped article is in crystallised or amorphous form. However, in the latter form, the articles generally have a rather low operating temperature ceiling and it is therefore generally preferred to have the matrix in the crystallised state. In order to ensure that the chain-extended poly(ethylene terephthalate) matrix is in this preferred form in the shaped articles, one or more of the following procedures may be adopted:

(1) The article may be shaped in a mould heated to at least 100°C and preferably 120°C to 170°C. Temperatures above 200°C are preferably avoided if degradation of the poly(ethylene terephthalate) is to be kept to a

minimum. The article should be kept in the mould for a sufficient time to allow crystallisation; times of from a few seconds to 2 to 3 minutes being generally adequate.

(2) Alternatively or additionally the shaped article may be subjected to a heat-treatment after shaping. Temperatures of from 120°C to 200°C are suitable and times of up to about 40 minutes are usually adequate.

(3) The composition may be kept as little as possible, e.g. not more than 10°C, above the melting point of poly(ethylene terephthalate) during the shaping process; e.g. in the barrel of the extruder or injection-moulding machine.

(4) A nucleating agent may be added to the composition before shaping so as to speed crystallisation, thereby reducing the residence time required in the hot mould, or the period required for the heat treatment. It has been found particularly desirable to include a nucleating agent in cases where a hot mould is used. The nature and amount of nucleating agent required to be effective depends to some extent upon the nature of the catalyst residues in the poly(ethylene terephthalate). If the polymer used contains a sufficient concentration of insoluble catalyst residues, no further nucleation may be required. If, on the other hand, the catalyst residues are soluble in the polymer, it is generally desirable to add a nucleating agent. The nucleating agent is preferably a very finely divided inorganic material. Talc and pyrophyllite have been found to be particularly effective, and may even enhance the nucleating effect of insoluble catalyst residues. Concentrations of from about 0.01 to about 2% are usually adequate, the particle size being preferably as fine as possible, e.g. 2 microns in size or less.

The nucleating agent may be added during the formation of the poly(ethylene terephthalate), or at any later stage.

All the components of the shaping composition are preferably kept as dry as possible because of the known deleterious effect of moisture upon molten poly(ethylene terephthalate). The composition is also kept as dry as possible and it is preferred to take steps to exclude moisture during the shaping process.

In addition to containing the poly(ethylene terephthalate), polyfunctional compound, rubbery material, and possibly nucleating agent, the compositions to be shaped may also include further components, if desired, for example, heat and light stabilisers, lubricants, dyes, pigments, mould release agents, and fillers, for example finely powdered metals, finely powdered metal oxides, graphite, carbon black, ground glass and molybdenum disulphide.

It is particularly preferred to include fibrous reinforcing agents, e.g. asbestos fibres and, especially, glass fibres. Where glass fibres are

incorporated, it is advantageous from the point of view of the physical properties of the shaped article to be formed to mix them with the poly(ethylene terephthalate) before the latter is contacted with the polyfunctional compound. The fibres may form, for example, from 5 to 60% by weight of the composition but preferred concentrations are from 20 to 40%. Short fibres are preferred.

Although the preferred use of our compositions lies in their conversion to thick-walled shaped articles by melt-shaping, especially injection-moulding, they may also be converted to other shaped article, e.g. filaments or fibres, if desired.

The invention is now illustrated by the following Examples in which all parts and percentages are by weight.

EXAMPLE 1.

90 Parts of dry poly(ethylene terephthalate) chip, of intrinsic viscosity 0.58 dl.g^{-1} , was tumble blended with 0.45 part of talc, 0.8 part of 4,4'-diisocyanatodiphenyl methane uretidione oligomer and 10 parts of a random poorly crystalline copolymer of ethylene (70.2% by weight) and methyl methacrylate (29.8% by weight) having a melt flow index at 190°C of 3.1 (ASTM Test D1238), a glass/rubber transition temperature of -33°C , a dynamic shear modulus of below 5×10^9 dynes/sq.cm, and a solubility parameter differing from that of poly(ethylene terephthalate) by at least 0.2.

The uretidione oligomer used in this and the following Example was prepared as follows: 4,4'-diisocyanatodiphenyl methane, which had been distilled under vacuum, was dissolved in dry chlorobenzene, and 4-dimethylaminopyridine (0.5 wt.% based on the diisocyanate) was added as a dimerisation catalyst. The pale yellow solution was stirred at room temperature for two hours and left overnight. The precipitated oligomer was

filtered off, washed with a little dry chlorobenzene and dried in a vacuum oven at 55°C .

The tumble blended mixture was then fed through a 3.20 cm. diameter screw extruder at a barrel temperature of 260°C and a screw speed of 60 r.p.m., the residence time in the barrel being about $1\frac{1}{2}$ minutes. The extrudate was quenched in cold water, granulated and dried in an air oven at 120°C overnight.

A portion of the extrudate was then extracted with o-chlorophenol, to separate the rubber from the ethylene terephthalate polymer which went into solution. The intrinsic viscosity of the ethylene terephthalate polymer was measured and is recorded in the Table below.

The extrudate was then injection moulded in a 2 oz Stübbe injection-moulding machine at a barrel temperature of 265°C , using a mould heated to 140°C and a cooling time of 30 secs. to give 51 mm. x 6 mm. x 3 mm. bars. The residence time in the barrel was about 3 minutes. Parts of several of the moulded product were extracted with o-chlorophenol to separate the rubber from the ethylene terephthalate polymer as described above. The intrinsic viscosity of the polymer in each was measured and the average value is recorded in the Table below.

The injection moulded bars were given a notch having a 0.254 mm radius, a 2.794 mm. depth and a 40° angle, cut into the 3 mm x 51 mm. edge, and the impact strengths determined at 22°C using a Hounsfield Charpy-type impact tester. The average result of a number of measurements is shown in the Table below.

By way of comparison, the above procedure was repeated using identical conditions and an identical composition except that the ethylene/methyl methacrylate copolymer was omitted. The results of tests on samples of this composition are given below.

Ethylene/methyl methacrylate copolymer present	Intrinsic viscosity of extrudate (dl.g^{-1})	Intrinsic viscosity of injection moulded product (dl.g^{-1})	Notched impact strength (kg.cm/cm^2)
No	0.726	0.60	2.58
Yes	0.800	0.84	3.63

By way of comparison, the notched impact strengths of articles containing unmodified poly(ethylene terephthalate) of intrinsic viscosity 0.60 and 0.84 would be about 2.2 and 2.9 kg. cm/cm².

EXAMPLE 2.

100 Parts by weight of poly(ethylene terephthalate) chip, of intrinsic viscosity 0.58 dl.g^{-1} , and 200 parts by weight of a random poorly crystalline copolymer of ethylene (92

wt.%) and β -hydroxymethyl methacrylate (8 wt.%), having a reduced viscosity of 1.7 (measured on a 1% solution in chloroform at 25°C), a glass/rubber transition temperature below 0°C, and a dynamic shear modulus of below 5×10^9 dynes/sq.cm., were blended in a 3.20 cm. diameter Iddon screw extruder at a barrel temperature of 260°C and a screw speed of 60 r.p.m., the residence time in the barrel being about 1½ minutes. 225 Parts by weight of this extrudate were then blended under similar conditions with a further 775 parts by weight of poly(ethylene terephthalate) chip, of intrinsic viscosity 0.58 decilitre/gram, to give an extrudate containing 15% by weight of copolymer, based on the total weight of extrudate.

The resulting extrudate was quenched in cold water, granulated and dried in an air oven overnight.

Portions of the extrudate were then introduced into a 2 oz Stübbe injection moulder

where they were mixed with talc (0.5% by weight based on the poly(ethylene terephthalate)) and varying proportions of the diisocyanate uretidione oligomer used in Example 1. The mixture was then injection moulded at a barrel temperature of 265°C using a mold temperature of 170°C and a cooling time of 30 secs. to give 51 mm x 6 mm. x 3 mm. bars. The residence time in the barrel was about 3 minutes.

Tests were carried out on the bars to determine the rubber particle sizes in the compositions (by optical microscopic examination), the percentage crystallinities of the compositions (using X-ray diffractometry), the intrinsic viscosities of the ethylene terephthalate polymer in the compositions, and the notched impact strengths of the bars (using 0.254 mm. radius notched samples as described in Example 1 on a Hounsfield Charpy-type impact tester). The results are tabulated below.

Uretidione oligomer, % by weight of mixture of poly(ethylene terephthalate) and rubber	Average rubber particle size μ	% crystallinity	Intrinsic viscosity (dl.g ⁻¹).	Notched impact strength (kg.cm/cm ²)
nil	4	45	0.52	2.1 (1)
1.5	5	46	0.74	5.9
2.0	5	41	0.76	7.1
2.5	4	47.6	0.86	8.7
2.5	4	47.6	0.99	11.5 (2)

The blends marked (1) and (2) were exhaustively extracted with cold o-chlorophenol and the insoluble material examined by infra-red spectroscopy. Poly(ethylene terephthalate) was detected in the residue from (2), but was not detected in the rubbery phase from (1).

By way of comparison, the notched impact strengths of articles moulded from unmodified poly(ethylene terephthalate) and having intrinsic viscosities corresponding to those listed in the Table above would be about 2.0, 2.6, 2.6, 3.0 and 3.3 kg. cm/cm².

EXAMPLE 3.

Dry poly(ethylene terephthalate) chip of intrinsic viscosity 0.65 dl.g.⁻¹ was tumble blended with a random, poorly crystalline, rubbery terpolymer having a melt flow index of 1.5, a glass/rubber transition temperature below 0°C and a dynamic shear modulus of less than 5×10^9 dynes/sq.cm., and comprising ethylene (77% by weight), β -hydroxyl meth-

acrylate (14% by weight) and methyl methacrylate (9% by weight), to give a mixture containing equal amounts of the two components. This mixture was fed through a 3.20 cm. diameter Iddon screw extruder at a barrel temperature of 250°C and a screw speed of 55 r.p.m. The extrudate was granulated and dried overnight in a vacuum oven at 140°C.

Portions of the extrudate were then extruded under the same conditions as those given above with dry poly(ethylene terephthalate) chip to give compositions containing, 1, 5, 15 and 25% by weight of the terpolymer.

These blends, together with the original blend containing 50% by weight of the terpolymer, were tumble blended with 2% by weight of 4,4'-diisocyanatodiphenyl methane (MDI) and injection moulded in a 2oz. Stübbe machine at a barrel temperature of 265°C, using a mould cooled to 20°C, to give 51

5 mm. x 6 mm. x 3 mm. bars. The bars were partially crystallised by subsequent heating at 140°C for 1 hour. The intrinsic viscosities of the ethylene terephthalate polymers in the moulded products were measured and are shown below.

The injection moulded bars were given a notch as is described in Example 1, and the

impact strength determined on a Hounsfield Charpy-type impact tester. Average results are quoted below. 10

An optical microscopic examination of the moulded blends was carried out to determine the size of the rubber particles. The results of tests are set out below. 15

Experiment	Terpolymer %, by weight of com- position	Intrinsic viscosity of moulded product (dl.g ⁻¹).	Average rubber particle size (μ)	Notched impact strength (kg.cm/cm ²)	Approximate residence time in barrel of moulder (minutes)
A	1	0.76	3	4.8	2
B	5	0.77	2	7.2	2
C	15	0.56	6	11.7	2
D	25	0.50	6	23.2	2
E	50	0.48	—*	17.8	not recorded

*Optical examination indicated that a part inversion of the rubber phase and the ethylene terephthalate polymer phase has occurred.

EXAMPLE 4.

20 The process of Example 3B was repeated but with the residence time in the barrel of the injection-moulding machine increased to 3½ minutes. The intrinsic viscosity of the ethylene terephthalate polymer in the moulded articles had increased to 0.97, the average rubber particle size was about 3 microns, and 25 the notched impact strength had risen to 8.9 kg. cm/cm².

EXAMPLE 5.

30 A mixture of equal weights of the poly-(ethylene terephthalate) and terpolymer used in Example 3 was prepared as described in that Example. Portions of this extrudate, when dried, were tumble blended with talc, more dry poly(ethylene terephthalate) chip, and various amounts of MDI, and re-extruded 35 as described in Example 3 to give blends containing 10% by weight of the terpolymer,

0.5% talc, based on the weight of the poly-(ethylene terephthalate), and 3,5 and 10% by weight (based on poly(ethylene terephthalate terpolymer) of MDI. The residence time of the material in the extruder was about 1½ minutes. 40

The extrudates were granulated, dried and injection moulded in a 2 oz Stübbe machine using a barrel temperature of 265°C, a mould heated to 140°C, and a cooling time of 48 seconds, in the mould, to give 51 mm. x 6 mm. x 3 mm. bars. The time spent by the material in the barrel of the machine was about 3½ minutes. The notched impact strengths of the bars, intrinsic viscosities of the ethylene terephthalate polymers, and the mean sizes of the rubber particles of the blends were determined as described hereinbefore. The results of these examinations are 55 tabulated below.

%, by weight of MDI.	Intrinsic viscosity of moulded product (dl g ⁻¹).	Average size of rubber particles (μ)	Notched impact strength (kg.cm/cm ²)
3	0.58	3-4	5.00
5	0.86	5	5.69
10	0.90	5	8.88

EXAMPLE 6.

80 Parts by weight of the dry poly(ethylene terephthalate) chip used in Example 3 were blended with 20 parts by weight of a dried melt-extruded blend containing equal weights of the same poly(ethylene terephthalate) and the terpolymer of ethylene, methyl methacrylate and β -hydroxymethyl used in Example 3, and extruded under the conditions described in that Example.

The extrudate was dried, granulated and tumble blended with 0.4% by weight of melittic trianhydride. Injection moulded, partially crystalline bars were prepared from this blend in the manner described in Example 3. The bars were examined as described above, and the results were as follows: the intrinsic viscosity of the ethylene terephthalate polymer was 0.50 dl.g^{-1} , the average Charpy notched impact strength of the bars was 4.1 kg.cm/cm^2 . The mean size of the dispersed rubber particles in the articles was between 4 and 5μ .

EXAMPLE 7.

522 Parts by weight of dry poly(ethylene terephthalate) chip of intrinsic viscosity 0.65 dl.g^{-1} were tumble blended with 478 parts by weight of glass fibres 6.3 mm long, and fed through a 3.20 cm diameter Iddon screw extruder at a barrel temperature of 265°C and a screw speed of 55 r.p.m. The extrudate was chopped and dried, and portions were tumble blended with various amounts of the blend described in Example 3 of equal weights of poly(ethylene terephthalate) and the terpolymer, and 0.5% by weight each of talc and MDI, and re-extruded in the Iddon extruder at 265°C and screw speed of 55 r.p.m. Under

these conditions, the time spent by the material in the extruder was about $1\frac{1}{2}$ minutes.

Blends were prepared in this manner containing 10% by weight of both glass fibre and terpolymer, 10% by weight of terpolymer and 25% by weight of glass fibre, and 15% by weight of terpolymer and 10% by weight of glass fibre. A further 2.5% by weight of MDI was added to each of these blends, which were then injection moulded using the conditions quoted in Example 5 to give both 51 mm. x 6 mm. x 3 mm. and 51 mm. x 9 mm. x 3 mm bars.

The size of the rubber particles, the intrinsic viscosity of the ethylene terephthalate polymer, and the Charpy notched impact strength were determined, in the manner previously described, for each blend. The flexural modulus of each blend was determined by bending the 51 mm. x 9 mm. x 3 mm. bars in a standard tensometer. The bar was placed with its larger faces horizontal in a three-point loading device in which flexure was effected by vertical movement of a pair of knife-edges 31.5 mm. apart, and in contact with the lower face of the bar, relative to a fixed knife-edge at the centre of the opposite face of the bar. The movement of the outer knife-edges relative to the central one was at a rate of 2.5 mm per minute. The modulus was calculated from the initial slope of the stress-deflection curve.

The results of these measurements are set out below. By way of comparison, measurements made on injection moulded samples that are similar to the above, except that the rubber and/or the glass fibre has been omitted, are also recorded.

Terpolymer (% by weight of the composition)	Glass fibre (% by weight of the composition).	Intrinsic viscosity of moulded product (dl.g^{-1}).	Average size of rubber particles (μ).	Notched impact strength (kg.cm/cm^2)	Flexural modulus (kg/cm^2).
10	10	0.99	5	10.6	2.44×10^4
10	25	0.82	3	10.3	4.00×10^4
15	10	0.85	5	8.5	2.36×10^4
10	0	0.86	5	5.7	1.78×10^4
0	0	0.96	—	3.1	2.60×10^4

EXAMPLE 8.

85 Parts by weight of dry poly(ethylene terephthalate) chip of intrinsic viscosity 0.65 dl.g^{-1} was tumble blended with 15 parts by weight of a copolymer designated EVA(1) and extruded, following the procedure of Example 3. The granulated, dried extrudate was

tumble blended with 2% by weight of MDI, injection moulded and subsequently crystallised by the method described in Example 3.

This process was repeated to obtain blends with various other copolymers identified below.

Tests were carried out on the prepared

mouldings of each blend to determine the intrinsic viscosity of the ethylene terephthalate polymer, the size of the rubber particles,

and the Charpy notched impact strength of the articles. The results are set out below.

5

Copolymer	Intrinsic viscosity (dl.g ⁻¹)	Average size of rubber particle (μ)	Notched impact strength (kg.cm/cm ²).
EVA(1)	0.87	4	6.6
EVA(2)	0.81	3—4	6.6
EEA(1)	0.80	6—7	7.3
EEA(2)	0.74	4—5	7.2

The rubbers used were as follows:

10 EVA(1): poorly crystalline copolymer of 74%, by weight of ethylene and 26% by weight of vinyl acetate, having a melt flow index at 190°C of 3.5, a glass/rubber transition temperature of -26°C and a dynamic shear modulus of less than 5 x 10⁹ dynes/sq.cm.

15 EVA(2): a poorly crystalline copolymer of ethylene (86%, by weight) and vinyl acetate (14%, by weight), having a melt flow index at 190°C of 2.0, a glass/rubber transition temperature below 0°C and a dynamic shear modulus of less than 5 x 10⁹ dynes/sq.cm.

20 EEA(1): a poorly crystalline random copolymer of ethylene (87%, by weight) and ethyl acrylate (13%, by weight) having a melt index at 190°C of 2.5, a glass/rubber transition temperature of -47°C and a dynamic shear modulus of less than 5 x 10⁹ dynes/sq.cm.

25 EEA(2): as for EEA(1) but containing 78% ethylene and 22% ethyl acetate, and having a melt flow index at 190°C of 18.5 and a glass/rubber transition temperature of -46°C.

EXAMPLE 9.

30 In each of a series of experiments 90 parts by weight of dry poly(ethylene terephthalate) chip (intrinsic viscosity 0.65 dl.g⁻¹) were blended with 10 parts by weight of a rubbery material identified below and extruded using a 3.20 cm. diameter Iddon screw extruder at a barrel temperature of 250°C and a screw speed of 70 r.p.m. The resulting extrudates were granulated, dried, and mixed with MDI in the proportions two parts by weight of MDI to 98 parts by weight of extrudate. The blends were injection moulded in a 2 oz. Stübbe machine in either of two ways, which were as follows.

45 A. Half a part by weight of talc was added to 100 parts by weight of the mixture. The blend was then injection moulded at a barrel temperature of 255°C a barrel residence time of 6 minutes, a mould temperature

of 140°C and a cooling time in the mould of 40 seconds.

50 B. The mixture was injection moulded at a barrel temperature of 255°C, a residence time in the barrel of 6 minutes, a mould temperature of 20°C and a cooling time of 5 seconds. The moulded articles were then annealed at 140°C for 1 hour to crystallise the ethylene terephthalate polymer.

55 Bars of dimensions 51 mm. x 6 mm. x 3 mm. were moulded by both methods. Tests were carried out on the bars to determine the rubber particle sizes (by optical examination), the intrinsic viscosity of the ethylene terephthalate polymer, and the notched impact strength of the bars (by the method described previously). The results are tabulated below.

60 The rubbery materials used, which were all at most only weakly crystalline and each of which had a glass/rubber transition temperature below 0°C and a dynamic shear modulus of less than 5 x 10⁹ dynes/sq.cm., were as follows:

65 *Experiment A:* a random copolymer of 74% by weight of ethylene and 26% by weight of vinyl acetate and in which at least 95% by weight of the vinyl acetate mers had been hydrolysed to vinyl alcohol. The melt flow index of the polymer was 1.0, measured at 190°C.

80 *Experiment B:* a random copolymer of 91% by weight of ethylene and 9% by weight of methacrylamide, having a melt flow index of 1.8, measured at 190°C.

85 *Experiment C:* a random copolymer of 70% by weight of ethylene and 30% by weight of methacrylic acid, having a melt flow index at 190°C of 8.9.

90 *Experiment D:* polyisobutylene having a Staudinger molecular weight of about 200,000.

Experiment E: a random copolymer of ethylene (62.5% by weight) and propylene (37.5% by weight), having a melt flow index at 190°C of 0.5.

Experiment F: a random copolymer of 60% 4-methyl and 5-methyl tetrahydroindenes, by weight of ethylene, 35% by weight of propylene and 5% by weight of a mixture of having an intrinsic viscosity measured in carbon tetrachloride at 25°C of 1.5.

Experiment	Intrinsic viscosity (dl.g ⁻¹)	Notched impact strength (kg.cm/cm ⁻²)	Average particle size μ .	Method of moulding
A	0.59	5.4	3	A
B	0.75	6.8	3	A
C	0.70	4.0	1—2	A
D	1.00	9.2	Oriented Fibrils up to 4 μ diameter	A
E	0.60	4.4	2—3	B
F	0.71	7.5	Ellipsoids aligned along flow direction.	B

EXAMPLE 10.

Experiment A. A dispersion of 15 parts by weight of terpolymer used in Example 3 in 85 parts by weight of the poly(ethylene terephthalate) used in Example 3 was prepared by first forming a 50/50 mixture and then adding further poly(ethylene terephthalate), as described in Example 3. The dried, granulated extrudate was then injection moulded in a 2 oz. Stübbe machine in the presence of 2% by weight of MDI, using a barrel temperature of 255°C, a residence time in the barrel of

6 minutes, a mould temperature of 20°C, and a cooling time in the mould of five seconds, to give bars of dimensions 51 mm. x 6 mm. x 3 mm. These were annealed for 1 hour at 140°C before being subjected to tests for notched impact strength, intrinsic viscosity of the ethylene terephthalate polymer and rubber particle size.

Experiment B. The process of Experiment A was repeated but omitting the MDI.

The results were as follows:

Experiment	Intrinsic viscosity (dl.g ⁻¹)	Notched impact strength (kg.cm/cm ²)	Average rubber particle size (μ)
A	0.55	13.3	5
B	0.55	4.0	5

EXAMPLE 11.

A dispersion of 10 parts by weight of the copolymer used in Example 9A and 90 parts by weight of poly(ethylene terephthalate) of intrinsic viscosity 0.65 dl.g⁻¹ was prepared by a single extrusion as described in Example 9. Talc (0.5% by weight) was then added to the dried, granulated extrudate and mouldings were prepared from the mixture, both with

and without the addition of 2% by weight of MDI. Injection mouldings in a 2 oz Stübbe machine were carried out at a barrel temperature of 255°C, a residence time in the barrel of 6 minutes, a mould temperature of 140°C, and a cooling time of 40 seconds. The mouldings (51 mm. x 6 mm. x 3 mm bars) were tested as in Example 10 and the results were as follows:

MDI present	Intrinsic viscosity (dl. g ⁻¹)	Notched impact strength (kg.cm.cm ⁻²)	Average Rubber particle size (μ)
No.	0.55	2.7	4
Yes	0.59	5.4	3

EXAMPLE 12.

The following blends were prepared to determine the effect of the rubber particle size on the impact strength of the blends. Both were prepared to contain 15% by weight of the terpolymer used in Example 3. Blend (A) was prepared by extruding together 15 parts by weight of rubber with 85 parts by weight of poly(ethylene terephthalate), 2 parts by weight of MDI and 0.5 part by weight of talc. A 3.20 cm diameter Iddon screw extruder was used at a barrel temperature of 265°C and a screw speed of 60 r.p.m., giving a residence time in the barrel of about 1½ minutes. The extrudate was granulated, dried and injection moulded in a 2 oz. Stübbe machine at a barrel temperature of 265°C, a residence time in the barrel of 3 minutes, a mould at 140°C and a cooling time in the mould of 48 seconds. The mouldings were 51 mm. x 6 mm. x 3 mm. bars.

Blend (B) was prepared by preparing a dispersion of equal weights of rubber and poly(ethylene terephthalate) and then adding further poly(ethylene terephthalate), using the double extrusion method described in Example 3. The extrudate was then mixed with 2% by weight of MDI and injection moulded in a Stübbe 2 oz. machine at a barrel temperature of 255°C, a residence time in the barrel of about 9 minutes, a mould at 20°C and a cool-in time in the mould of five seconds to give bars of dimensions 51 mm. x 6 mm. x 3 mm. The bars were annealed at 140°C for 1 hour to crystallise the ethylene terephthalate polymer.

The mouldings from (A) and (B) were tested for intrinsic viscosity of the ethylene terephthalate polymer, and notched impact strength, and were optically examined to determine the quality of the rubber dispersion. The results were as follows:

Experiment	Intrinsic viscosity (dl.g ⁻¹)	Notched impact strength (kg.cm/cm ⁻²)	Range and average size of rubber particles.
A	0.57	4.5	1—350 μ, mean greater than 20μ.
B	0.55	13.2	1—30 μ, mean about 5μ.

EXAMPLE 13.

A dispersion in poly(ethylene terephthalate) having an intrinsic viscosity of 0.65 dl.g⁻¹ of 10% by weight of the terpolymer used in Example 3 was prepared by the double extrusion method described in that Example. The extrudate was injection moulded in a 2 oz. Stübbe machine with 2% by weight of MDI to give discs 11.4 cm. diameter and 3 mm. thick the sprue being edge on to the circumference of the disc. The barrel temperature of the moulder was 255°C and the residence time about 9 minutes, the mould was at 20°C and the cooling time was 20 seconds. The discs were annealed for 1 hour at 140°C. Bars 50 mm. x 6 mm. x 3 mm. were cut from the discs with the long axis either parallel or perpendicular to the direction of flow of the polymer in the mould during injection. These

were tested for notched impact strength in the manner already described. The results were as follows:

	Notched impact strength (kg. cm/cm ²)
Axis parallel to flow	9.3 ± 1.0
Axis perpendicular to flow	8.0 ± 1.0

EXAMPLE 14.

A series of dispersions in poly(ethylene terephthalate) of the ethylene/methyl methacrylate/β-hydroxyethyl methacrylate terpolymer used in Example 3 were prepared by the double extrusion method described in that Example. Dispersions containing 5, 10 and 15% by weight of the terpolymer were prepared. These were tumble blended with 2% by weight of MDI and injection moulded in

5 a 2 oz. Stübbe machine to give bars of dimensions 51 mm. 6 mm. x 3 mm. The barrel temperature was 255°C and the mould temperature 20°C. The cooling time was 5 seconds and a series of residence times in the barrel were used. Samples were annealed for 1 hour at 140°C before testing. The intrinsic viscosity of the ethylene terephthalate polymer, the notched impact strength of the bars, and the mean size of the rubber particles in the blends were determined and the results are tabulated below. 10

% by weight of rubber.	Residence time in barrel (secs)	Intrinsic viscosity (dl.g ⁻¹).	Charpy notched impact strength (kg.cm/cm ²)	Mean diameter of rubber particles μ
5	140	0.77	7.3	2
5	310	0.96	10.3	2
5	525	0.98	10.0	2
5	735	1.0	9.7	2
10	105	0.79	9.5	3
10	210	0.82	10.2	3
10	350	0.82	10.7	3
10	525	0.83	10.6	3
10	700	0.70	9.2	3
15	105	0.55	13.5	4
15	210	0.67	13.8	4
15	350	0.60	13.3	4
15	525	0.55	13.4	4
15	700	0.52	11.6	4

WHAT WE CLAIM IS:—

15 1. A melt-shapable polymer composition comprising

- (i) poly(ethylene terephthalate),
 (ii) a rubbery material comprising at least one amorphous or poorly crystalline high molecular weight synthetic polymer or copolymer which is substantially insoluble in poly(ethylene terephthalate) so as to form a discrete dispersed phase therein and which has a glass/rubber transition temperature below 0°C and dynamic shear modulus not greater than 5×10^9 dynes/sq.cm. and
 (iii) at least one polyfunctional compound selected from
 20
 25
 30 (a) compounds which are capable of reaction with at least two groups

selected from —OH and —COOH groups contained in (i), under the conditions of the melt shaping process, and

- (b) compounds which under the conditions of the melt shaping process are dissociable to compounds of type (a) 35

and wherein the rubbery material forms from 1 to 50% of the total weight of (i), (ii) and (iii). 40

2. A composition as claimed in claim 1 in which the rubbery material is capable of reaction with the polyfunctional compound under the conditions of the melt shaping process. 45

3. A composition as claimed in claim 2 in which the rubbery material contains hydroxyl groups.

4. A composition as claimed in claim 3 in which the rubbery material is a copolymer of ethylene with comonomeric material which includes at least one hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid.
5. A composition as claimed in claim 3 in which the rubbery material is selected from rubbery copolymers of ethylene with at least one of 2-hydroxy-n-propyl methacrylate and hydroxyisopropyl-methacrylate, rubbery copolymers of ethylene and 2-hydroxyethyl methacrylate and rubbery copolymers of ethylene with methyl methacrylate and at least one of 2-hydroxy-n-propyl methacrylate and hydroxyisopropyl methacrylate.
6. A composition as claimed in any of claims 1 to 5 in which the polyfunctional compound is selected from polyisocyanates, uretidione dimers of polyisocyanates and higher molecular weight uretidione oligomers of polyisocyanates.
7. A composition as claimed in claim 6 in which the polyisocyanate is 4,4'-diisocyanatodiphenylmethane.
8. A composition as claimed in any of claims 1 to 7 which also contains a nucleating agent for the poly(ethylene terephthalate).
9. A composition as claimed in any of claims 1 to 8 which also contains glass fibres.
10. A composition as claimed in any of claims 1 to 9 in which the rubbery material forms from 5 to 35% of the total weight of (i), (ii) and (iii).
11. A composition as claimed in claim 10 in which the rubbery material forms from 5 to 15% of the total weight of (i), (ii) and (iii).
12. A composition as claimed in any of claims 1 to 11, in which the polyfunctional compound forms from 0.05% to 10% of the total weight of (i), (ii) and (iii).
13. A composition as claimed in claim 12 in which the polyfunctional compound forms from 0.5% to 5% of the total weight of (i), (ii) and (iii).
14. A composition as claimed in claim 9 in which the glass fibres form from 20 to 40% by weight of the composition.
15. A composition as claimed in claim 1, substantially as described.
16. A composition as claimed in claim 1, substantially as shown in Examples 1 and 2.
17. A composition as claimed in claim 1, substantially as shown in Examples 3 to 14.
18. A method of producing a composition as claimed in any of claims 1 to 17 which includes the step of subjecting a mixture of poly(ethylene terephthalate) the rubbery material and the polyfunctional compound to conditions of shear at a temperature above the melting point of the poly(ethylene terephthalate).
19. A method as claimed in claim 18 in which the polyfunctional compound is added to the poly(ethylene terephthalate) after the latter has been mixed with the rubbery material and the glass fibres, if any.
20. A method as claimed in claim 19 in which the poly(ethylene terephthalate) is extruded with the rubbery material and optionally glass fibres and the extrudate is then extruded with the polyfunctional compound.
21. A method as claimed in claim 18 substantially as described.
22. A method as claimed in claim 18 substantially as shown in Examples 1 and 2.
23. A method as claimed in claim 18 substantially as shown in Examples 3 to 14.
24. A composition obtained by the method claimed in any of claims 18 to 23.
25. A process for the production of a shaped article of ethylene terephthalate polymer having improved impact strength which comprises forming and melt shaping a composition as claimed in any of claims 1 to 17 and 24 to yield a shaped article comprising a matrix of ethylene terephthalate polymer and a disperse phase comprising finely dispersed discrete particles of the rubbery material in said matrix.
26. A process as claimed in claim 25 which includes the step of causing or allowing the ethylene terephthalate polymer matrix in the shaped article to crystallise.
27. A process as claimed in claim 25 or claim 26 in which the composition is injection moulded.
28. A process as claimed in any of claims 25 to 27 in which the poly(ethylene terephthalate) is subjected to temperatures in the range 255°C to 290°C for a period of from ½ minute to 15 minutes while in the presence of the polyfunctional compound.
29. A process as claimed in claim 25, substantially as described.
30. A process as claimed in claim 25, substantially as shown in Examples 1 and 2.
31. A process as claimed in claim 25, substantially as shown in Examples 3 to 14.
32. A shaped article obtained by the process of any of claims 25 to 31.
33. A shaped article of material comprising an ethylene terephthalate polymer matrix and a discrete rubbery disperse phase, and wherein the matrix comprises macromolecular units each formed of at least two polymeric chains at least 90% of the mers in which have the structure $\text{—OCH}_2\text{CH}_2\text{OCOArCO—}$ where Ar represents a para-phenylene group each chain being linked to another chain by a chemically different mer which is the polyvalent residue of a polyfunctional compound which is capable of reaction with at least two groups selected from —OH and COOH groups contained in poly(ethylene terephthalate), the disperse phase comprises finely dispersed particles of a rubbery material comprising at least one amorphous or poorly crystalline high molecular weight synthetic polymer or copolymer which has a glass/rubber transition temperature below 0°C and a dynamic shear

- modulus of less than 5×10^9 dynes/sq.cm. and is reactive with the polyfunctional compound, and the rubbery material is grafted to the ethylene terephthalate polymer matrix by means of polyvalent residues of the polyfunctional compound and forms from 1 to 50% of the total weight of the matrix and disperse phase.
- 5 34. A shaped article as claimed in claim 33 in which the rubbery material forms from 5 to 35% of the total weight of the matrix and disperse phase.
- 10 35. A shaped article as claimed in claim 34 in which the rubbery material forms from 5 to 15% of the total weight of the matrix and disperse phase.
- 15 36. A shaped article as claimed in any of claims 33 to 35 which contains glass fibres.
- 20 37. A shaped article as claimed in claim 36 in which the glass fibres form from 20 to 40% by weight of the article.
- 25 38. A shaped article as claimed in any of claims 33 to 37 in which the ethylene terephthalate polymer matrix is at least partially crystallised.
39. A shaped article as claimed in any of claims 32 to 38 in which the average size of the particles of the disperse phase is not greater than 10 microns.
40. A shaped article as claimed in any of claims 32 to 39 in which the matrix has an intrinsic viscosity, measured on a solution of the polymer in o-chlorophenol at 25°C, of at least 0.5 decilitre gram⁻¹.
- 30 41. A shaped article as claimed in claim 40 in which the intrinsic viscosity of the matrix is from 0.65 to 0.85 decilitre gram⁻¹.
- 35 42. A shaped article as claimed in claim 32 or claim 33, substantially as described.
- 40 43. A shaped article as claimed in claim 32 or claim 33, substantially as shown in Examples 1 and 2.
- 45 44. A shaped article as claimed in claim 32 or claim 33, substantially as shown in Examples 3 to 14.

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